THE SOLUBILITY OF OXYGEN.

An analytical method for the determination of the solubility of oxygen under different conditions.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy,
in the Faculty of Pure Science,
Columbia University.

BY

ALAN H. RICHARDSON, B.S.

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THE SOLUBILITY OF OXYGEN.

I. OBJECT OF THE RESEARCH.

This research was undertaken to answer two important questions,

(a) Are the results of analytical methods the same as those obtained by a method depending upon the measurement of the loss of volume of a gas when brought into intimate contact with water? and,

(b) Is the amount of a gas dissolved by a liquid dependent upon the hydrostatic pressure in the liquid as well as upon the gaseous pressure?

II. HISTORICAL.

Much work has been done by many investigators on the amount of oxygen dissolved in water under various conditions. The method most used has been that of Winkler, first introduced by him in 1888.[1] Air containing 20.96% of oxygen was used by Winkler as his source of oxygen. He calculated what the solubility of oxygen would be if present alone, using the Laws of Dalton and of Henry. Winkler has continued to experiment with his method. In 1889 [2] he improved the original method by advocating certain changes in the concentration of the reagents. In this work the error due to the oxygen dissolved in the reagent was found to be negligible. In this work also at this time he introduced the idea that hydrostatic pressure would have an effect on the solubility of the gas. His essential statement was that the amount of oxygen which water can absorb is dependent upon the height of the column of water. He suggested that it was best to calculate the solubility of gases in terms of a column whose height was zero. One-half the pressure of the water column was added to the barometer reading, the sum being considered as the total pressure of the solution.

Müller[3] used Winkler's procedure but instead of manganese chloride, used manganese sulfate in a different type apparatus, but the advantages did not seem an especial improvement.

Romijn (1896) [4] introduced an apparatus for collecting samples of water for analysis. It was a pipette with stop cocks at either end and a funnel on one end. He introduced Rochelle Salts for the purpose of keeping the manganese salts in solution. There does not seem to be any advantage of this method over the original method.

Many others have used the method with but slight modification, for the amount of oxygen dissolved in natural waters. Many modifications have been made in order to overcome the interfering substances in natural waters such as iron salts, nitrates, nitrites, etc. Most of the work has been done with varying types of apparatus used for sampling the waters.[5, 6, 7, 8, 9]

A "micro" Winkler method has also been worked out by Winkler and by Lund.[10, 11]

Theriault [12] has made an investigation of the method and its modifications rather completely. His results are comparative only. The most use for the method has been in the determination of the amount of oxygen present in natural waters and not for the determniation of the solubility of oxygen in pure water.

Other analytical methods have been in use for the determination of oxygen in water. The Schützenberger Method [13] where sodium hydrosulfite is used for titration is tedious, long and more complicated than the Winkler method. From the results of workers, it is claimed to be not as accurate as the Winkler Method. Roscoe and Lunt [14] have done work on the Schützenberger Method.

The Mohr Method [15] uses the ferrous ion in alkaline solution, then titrating the excess ferrous ion. This method is difficult to manipulate and compared with the Winkler method, is inferior.

For simplicity, accuracy and general use the Winkler method seems far superior to any analytical method advocated for the determination of the amount of oxygen dissolved in water.

III. THE WINKLER METHOD.

The method as first used was as follows:

$MnCl_2.4H_2O$. Dissolve 40 grams in 100 cubic centimeters of water. Approximately 2N.

NaOH — KI. Dissolve 50 grams of pure NaOH in 100 cubic centimeters of water. In this was dissolved 20 grams of potassium iodide thereby making in each centimeter approximately 0.5 gram of potassium iodide.

HCl concentrated.

$Na_2S_2O_3$ — 0.01 Normal.

Flasks with large gutters, such as used in the iodine number determinations in fat and oil analysis were used. The flasks were calibrated so that when completely filled and the glass stoppers were inserted, the contents of the flasks were known exactly. No air bubbles were left in the flask. Water could be placed in the gutter during the settling of the precipitate so that no air bubbles could enter upon standing. The iodine flasks were not used by Winkler. They were used here because of greater convenience and because they served to keep the air from entering the flask after precipitation had occurred.

After passing the air through soda lime to purify it of any carbon dioxide present, it was bubbled through the water in the flasks. The reagents were added by means of pipettes, delivery being made at the bottom of the flasks. One cubic centimeter of the alkaline potassium iodide solution was added and then one cubic centimeter of the manganese chloride solution. On adding the latter solution a precipitate was formed which was oxidized by the oxygen in solution. The flasks were then restoppered with no air bubbles remaining, and shaken to ensure oxidation of the precipitates by the oxygen in solution. The precipitates were allowed to settle after

which the solutions were acidified with two cubic centimeters of the hydrochloric acid. The stoppers were again replaced and the precipitates dissolved by shaking the flasks. This reaction liberated an amount of iodine equivalent to the oxygen present. The solutions were then transferred to a beaker and titrated with standardized thiosulfate solution. Each cubic centimeter of the thiosulfate being equivalent to a definite amount of oxygen, the amount of oxygen dissolved could be calculated.

The formula for calculations was as follows:

$$\text{Grams of oxygen per liter} = \frac{\text{cc. thiosulfate} \times \text{Grams of } O_2 \text{ equiv. to 1 cc. of thiosulfate} \times 760 \times 1000}{\text{barometer corrected} \times \text{volume of liquid in flask}}$$

IV. DEVELOPMENT OF A MODIFIED WINKLER METHOD FOR OXYGEN.

1. Materials.

Reagents: The sodium hydroxide used was by alcohol and of high purity.

The potassium iodide used was that from Eimer and Amend of tested purity.

The manganese sulfate was of Eimer and Amend tested purity. The formula contains four molecules of water of hydration.

The sulfuric acid was 9 Molar made from Baker & Adams pure concentrated acid.

Gas Free Water. The water was that from the distilled water tap of the Havemeyer Laboratories. The water was placed in a two liter pyrex balloon flask to which was attached a reflux condenser. The water was boiled under the reflux condenser for a period of one-half to one hour. During this boiling there was a condensed portion of the liquid in the condenser which vibrated vertically in the condenser thus preventing any contact of the boiling liquid with air. The gas free water was siphoned under suction from the two liter bal-

loon pyrex flask to a one liter pyrex balloon flask while still boiling, thereby causing very violent ebullition. The one liter flask had a two hole stopper in which there was the lead-in from the two liter flask and a 100 cubic centimeter pipette. The pipette and flask were filled with water thereby preventing the oxygen dissolving and diffusing into the lower part of the liquid from which the water was taken for the saturation. When the flask and pipette were completely filled the connecting rubber tube from the two liter flask was clamped by a screw-clamp after the suction was removed, thereby maintaining the water in the one liter flask and pipette. The water was cooled and used as gas free water. An analysis was made on a sample of gas free water and 0.0000006 gram of oxygen was found in a liter of the solution. It represents the amount of oxygen in the gas free water plus the reagents and is in reality a blank determination.

The oxygen was obtained from a large supply tank. A constant composition was obtained by the one source of supply. Due to work previously done[16] on the same supply in this laboratory, by passing through pre-heaters, soda lime and concentrated sulfuric acid, and in general the method and apparatus used in organic combustions, it was found that the oxygen was sufficiently pure to omit all pretreatment. The purity of the oxygen was further tested using generated oxygen by heating potassium chlorate in the presence of manganese dioxide as a catalyst. The generated oxygen, dissolved in water, gave identical results with the oxygen which came from the supply tank.

2. Methods of Saturation.

Large bubbles of oxygen were passed through flasks of the type used in iodine number determinations in the analysis of fats and oils. Results obtained were lower than those given for the solubility of oxygen at 760 mm. as reported in the literature.

By noting the quantity found in Table 1 it could be seen that the solubility was considerably lower than the Winkler

value. It indicated that there was a possibility that saturation was insufficient. From previous experience in this laboratory with an apparatus designed [17] for determining solubilities, saturation could be obtained in two to three hours. The time of saturation was varied and it was found that with increase in time from two hours to six hours, there was an increase in the value obtained. The results either indicate the failure of the method or the failure to get saturation.

TABLE 1.

Gr. O_2 per liter	Winkler Value
.0250	.03945
.0237	.03945
.0228	.03945
.0219	.03945
.0219	.03945
.0291	.03945
.0305	.03945
.0333	.03945
.0303	.03945
.0293	.03945

Temperature 25° C.

If there were *smaller bubbles* more surface would be presented to the liquid and hence saturation would be reached in a shorter time. There was the possibility of supersaturation, if the bubbles were too small. The two methods of saturating were compared—small and large bubbles being used. A capillary tube was drawn out to a jet. The jet was placed close to the bottom of the flask. When the bubbles issued from the capillary they were immediately split up into a spray of fine bubbles. Saturation was conducted for the same length of time with a small jet without the spraying effect and it was found that saturation in the latter case was obtained more rapidly. The value was below the value reported by Winkler. Saturation was not obtained due to the fact that the stirring is lessened with smaller bubbles.

Stirring the water while the bubbles were being passed through was tried. This did not change the solubility. To ensure better stirring a different type vessel was used. A long column of liquid through which the bubble travelled would furnish an ideal vessel for saturation. An ordinary *bomb tube*, as used in organic combustions was resorted to. Several determinations were carried out with this tube but the value was lower than Winkler's reported value. Graduated cylinders were also tried for the saturating vessel. *A tall narrow cylinder* capable of giving several samples was used for saturating. The oxygen was introduced in large bubbles at the bottom of the cylinder. This form of apparatus did not give higher results.

Shaking the water with the gas was tried with the result that there seemed to be no difference in the solubility of oxygen when shaken and when bubbles were used. Cady[18] suggested that there would be a higher value obtained for the solubility of a gas when saturation was obtained by shaking. The reason assigned for this difference was that as the liquid and gas were shaken the impact of the water on the glass, thereby including bubbles of gas, forces the gas into solution at a higher pressure than measured. However, results showed no difference in the two methods of saturating. The results were not higher when shaking was used. Saturating at higher pressure was tried thereby getting a supersaturated solution when reduced to normal pressure. Dissolving was done by shaking. All results were lower than the Winkler solubility. All results of shaking were from eight to ten percent lower.

An apparatus was set up whereby the amount which dissolved could be measured. The amount of oxygen dissolved was determined analytically and compared with the measured amount. Table 2. In all cases the amount by analysis was less than the amount measured. From these results it was quite evident that the method used could not be applied to oxygen unless some modification in the procedure was introduced. All the oxygen was not being analytically determined.

TABLE 2.

Amount of oxygen measured	Amount of oxygen by Analysis
.00721	.00710
.00681	.00675
.00690	.00643
.00663	.00608
.00757	.00697
.00671	.00662
.00885	.00798
.00799	.00753
.00743	.00700

3. Standardization of thiosulfate solution was done against twice recrystallized potassium dichromate. This seemed about as accurate and as convenient as any method in common use. It was also decided to use standard potassium permanganate solution, standardized against Bureau of Standards sodium oxalate and according to their recommendations. The method of standardizing the thiosulfate was modified by H. T. Beans[19] and co-workers. The difference in the standardization of thiosulfate was not sufficient to change results but the latter method seemed by far the best from the results obtained.

4. The concentrations of reagents specified by Winkler for a determination was more than sufficient for water saturated with oxygen. The concentration of the potassium iodide was investigated. Amounts of 0.07, 0.15, 0.4, 0.5, 0.6, 0.66, 0.75, 1.5 grams were used in the flasks as in Table 3. As the concentration of the potassium iodide increased, there seemed to be no definite relationship between the amount of the oxygen found and the amount of the potassium iodide added. Concentrations of potassium iodide from 0.07 grams to 1.5 grams in approximately 300 cubic centimeters seemed to have no noticeable effect. By adding two cubic centimeters of the sodium hydroxide and manganese sulfate, the results were higher than those obtained when one cubic centimeter was used.

TABLE 3.

Varying concentrations of iodide with one cubic centimeter of sodium hydroxide and manganese sulfate.

Grams of Potassium Iodide	Temp.	Grams O_2 per liter	Grams O_2 reported by Winkler
0.07	25	0382	0408
0.07	25	0370	0408
0.40	25	0389	0408
0.40	25	0387	0408
0.40	25	0385	0408
0.40	20	0412	0444
0.40	20	0419	0444
0.40	20	0417	0444
0.50	19	0431	0452
0.50	19	0425	0452
0.50	19	0420	0452
0.60	21	0348	0437
0.60	21	0390	0437
0.60	21	0406	0437
0.66	25	0372	0408
0.66	25	0368	0408
0.66	25	0384	0408
0.75	25	0379	0408
0.75	25	0377	0408
1.50	21	0324	0437
1.50	21	0336	0437

If it takes one cubic centimeter of sodium hydroxide and manganese sulfate when air is used as the source of oxygen and the oxygen concentration in these solutions was five times the amount, then five times the amount of reagents should be used for oxygen. Solubilities were obtained which were closely in agreement with the solubility which Winkler reported. In Table 4 are the results of these solubilities. Although these results may be considered good there is a general tendency for the solubilities to be a little less than the Winkler value.

It was noticed that when about to titrate and while transfering the solution, after the iodine had been liberated, into an open beaker to titrate, there was a perceptible odor of iodine. A measured amount of the solution containing the

TABLE 4.

Grams O_2 per Liter	Winkler Value at 25° C.
.04025	.04080
.04045	.04080
.03993	.04080
.04025	.04080
.04065	.04080
.04025	.04080
.04014	.04080
.04025	.04080
.04035	.04080

free iodine was taken from the flasks in which all operations had been carried out and the remaining iodine in the flask was then titrated. Theriault [12] suggested this procedure. In this manner the iodine solution was disturbed only to a very slight extent. With air this procedure gave very good results.

TABLE 5.

Grams O_2 per Liter	Value by Winkler
.00826	.008211
.00826	.008211
.00821	.008211
.00820	.008211
.00827	.008211
.00825	.008211
.00826	.008211
.00822	.008211
.00823	.008211
.00829	.008211
.00818	.008211
.00820	.008211
.00819	.008211
.00820	.008211
.00825	.008211
.00821	.008211
.00825	.008211
.00817	.008211
.00817	.008211

TABLE 5—Continued

Grams O_2 per Liter	Value by Winkler
.00822	.008211
.00822	.008211
.00822	.008211
Av. .00824	
a. d. $.0_4 25$	
A. D. $.0_5 79$	

Temperature of saturation 25° C.

The method used was as follows: One cubic centimeter of the reagents, manganese sulfate and sodium hydroxide of concentration as suggested by Winkler was used. Saturation was secured by shaking with air. Two cubic centimeters of concentrated sulfuric acid were used to acidify. After the precipitate had settled and the acid added to liberate the iodine, fifty cubic centimeters of this iodine solution were withdrawn by pipette. In this way the iodine solution remaining in the flask could be titrated without disturbing the solution while transferring it to another vessel.

The above method as modified was applied to the determination of oxygen, using five times the amount of reagents. The same amount of reagents could be used for oxygen as for air and there still would be plenty of reagent. Using this above modification with oxygen, the solubilities still continued low. The method was carried out in exactly the same manner, that is to say, by titrating in the flasks in which the original saturation took place.

The iodine vaporization seemed to be the chief cause of the trouble. Solutions after the iodine had been liberated, were placed in cooling baths of salt and ice and titrated therein. This cut down the error still more. When cooling with ice was tried with oxygen, the results were not as satisfactory.

The concentration of the potassium iodide was increased enormously as another means of holding the iodine in solution. Instead of a maximum of one and a half grams as had

heretofore been added, ten cubic centimeters of a saturated solution of potassium iodide was added. Potassium iodide is soluble to about one gram per cubic centimeter. By adding ten cubic centimeters of the saturated solution of potassium iodide it was found that the solubility of oxygen was obtained which was the nearest to the Winkler value thus far obtained.

To show the effect that the concentration of the potassium iodide has upon the solubility value of the oxygen, various concentrations were added. When the concentration of the potassium iodide was increased the figure for the solubility was increased. The general tendency was toward an increase. The increase was not due to the fact that more oxygen was introduced in the reagent for it had been shown previously that gas free water with the reagents contained such a small amount of oxygen that any difference could not be attributed to an increase in the number of cubic centimeters of potassium iodide added. Hence this was due to the greater power of the potassium iodide holding the iodine in solution. In Table 6 five cubic centimeters were used for the sodium hydroxide and manganese sulfate.

TABLE 6.

cc. of Sat. KI		Grams of KI	Grams of O_2 per Liter
1	—	1.328	.0394
1	—	1.328	.0395
1	—	1.328	.0393
1	—	1.328	.0394
2	—	2.656	.0394
2	—	2.656	.0393
2	—	2.656	.0394
2	—	2.656	.0394
3	—	3.984	.0390
3	—	3.984	.0391
3	—	3.984	.0392
3	—	3.984	.0392
4	—	5.312	.0395
4	—	5.312	.0395
4	—	5.312	.0389
4	—	5.312	.0384

TABLE 6—Continued

cc. of Sat. KI		Grams of KI	Grams of O_2 per Liter
4	—	5.312	.0390
4	—	5.312	.0390
4	—	5.312	.0397
5	—	6.640	.0395
5	—	6.640	.0396
6	—	7.968	.0397
6	—	7.968	.0397
7	—	9.296	.0398
7	—	9.296	.0400
7	—	9.296	.0397
7	—	9.296	.0397
8	—	10.624	.0395
8	—	10.624	.0399
8	—	10.624	.0400
8	—	10.624	.0398

Table 6 gives the results showing the grams of oxygen per liter increasing with the increasing concentration of the potassium iodide.

Various amounts of *sodium hydroxide* and *manganese sulfate* were tried to determine their effect on the value of the solubility of oxygen. From Table 7 it can be seen that as the amount of reagents added becomes larger the number of grams of oxygen per liter becomes larger. The values in Table 6 and 7 cannot be considered as the true value for the solubility of

TABLE 7.

cc. of NaOH & $MnSO_4$	Grams O_2 per Liter
2	.0385
2	.0389
2	.0391
3	.0393
3	.0391
3	.0395
3	.0395
4	.0395
4	.0397
4	.0397
5	.0395
5	.0396
5	.0397

oxygen. The results merely represent the effect that the various concentrations have upon this value.

5. Carlson's Work.[20]

Carlson claims to have used the original Winkler Method for oxygen with satisfactory results which he gave as follows:

At 17° and 758 mm. pressure.	
cc. of O_2 per liter	Grams of O_2 per liter
32.171	.04594
32.180	.04595
32.188	.04597
32.209	.04600
32.175	.04594

This work was duplicated using the concentrations which he used namely: Two cubic centimeters of twelve normal sodium hydroxide, and ten percent potassium iodide, two cubic centimeters of manganese chloride, ($MnCl_2, 4H_2O$), eighty grams in 100 cubic centimeters of water, and five cubic centimeters of concentrated hydrochloric acid.

The results were similar to those which were obtained in the first part of the work.

Grams of O_2 per liter at 25°	
.0345	Winkler Value — .0408
.0349	

By referring to Tables 1, 2, 3, solubilities given show further indication of the method not applying.

V. THE SOLUBILITY OF OXYGEN BY THE MODIFIED WINKLER METHOD.

Saturation was obtained by shaking water with oxygen in a short neck liter balloon flask. An atmosphere of oxygen was obtained over the water by having a small stream of bubbles flowing through the flask. The oxygen outlet of the flask was connected with a water trap to ensure against any backward diffusion of air thereby causing oxygen to be contaminated. The water in the flask with the atmosphere of oxygen above it

was placed in a thermostat regulated to twenty-five degrees. Ten to fifteen minutes were allowed for the water to assume the temperature of the bath. The flask was shaken by hand, keeping it in the thermostat while shaking. It was found by this method that saturation could be obtained in at least five minutes. Fifteen to thirty minutes were usually allowed for the saturation and then ten to fifteen minutes more allowed for the solution to remain at rest and attain equilibrium. The flask was then taken from the thermostat and the contents siphoned into iodine flasks. These flasks were calibrated so that when the stoppers were inserted the contents of the flask would be known. During the siphoning process the outlet of the siphon was kept below the water level so that there would be as little exposure to the air as possible in transferring from one vessel to another and the disturbance of the solution reduced to a minimum.

The reagents were then added. The manganese sulfate solution was made by dissolving 48 grams of the $MnSO_4 \cdot 4H_2O$ in one hundred cubic centimeters of distilled water. The sodium hydroxide solution was made by dissolving fifty grams of sodium hydroxide in one hundred cubic centimeters of distilled water. The potassium iodide was not placed in this solution. A separate saturated solution of potassium iodide was made fresh for every determination in order that iodine would not be liberated while standing.

Five cubic centimeters of potassium iodide solution were added from a pipette, delivery being at the bottom of the flask. This made the concentration of potassium iodide about a 4% solution. This enabled the saturated solution to remain at the bottom due to its heavy specific gravity. Five cubic centimeters of sodium hydroxide were introduced in the flask in the same manner as the potassium iodide. Five cubic centimeters of the manganese sulfate solution were added next. A creamy precipitate formed immediately in the bottom of the flask on addition of the latter reagent. The creamy precipitate which was first formed gradually changed to dark brown due to the oxidation by the oxygen dissolved in the water. Before disturbing the flask, the stopper had to be inserted. This was

done in such a manner so that no air bubble was caught in the flask but that it was completely filled with liquid and precipitate. The flask was shaken about five minutes to ensure complete mixing of the precipitate with the solution. The precipitate settled very quickly due to the presence of excess of the reagents. The flasks were shaken a second time and the precipitate allowed to settle. This was done until the precipitate had settled three times. After a period of an hour after the last settling, the solutions were acidified with ten cubic centimeters of sulfuric acid. This sulfuric acid was introduced in the flasks, delivery being near the precipitate at the bottom of the flask, so as to cause as little stirring as possible and thereby preventing the precipitate from reaching the surface by agitation and being oxidized further by the oxygen in the air. The acid concentration was approximately 0.6 M. The stopper was again inserted and the flask shaken to mix the acid with the solution. After standing five minutes the stopper was removed and one hundred cubic centimeters of the iodine solution was drawn off by pipette. The solution remaining on the stopper was washed into the flask. The iodine was titrated with standard sodium thiosulfate. The titration was completed using starch as an indicator near the end of the titration.

The number of grams of oxygen equivalent to one cubic centimeter of the standard thiosulfate was known. From this was calculated the number of grams of oxygen in solution.

Concentration of reagents in the flasks.

$NaOH = .20$ M. $MnSO_4 \cdot 4H_2O = .15$ M.
$H_2SO_4 = 0.6$ M. $KI = 4\%$

1. Precautions.

The number of cubic centimeters of reagents added to each of the flasks before and during precipitation is fifteen. This amount had to be subtracted from the total volume of the flasks. The one hundred cubic centimeters of iodine solution which was taken from the flask just before titrating with the thiosulfate was subtracted. From previous work by Winkler and a further checking on this work, the reagents could be con-

sidered oxygen free and therefore the reason for subtracting their volumes from the solution.

While the precipitate was standing, the gutter around the stopper was filled with water to prevent any air seeping between the stopper and the walls of the flask.

All reagents were introduced near the bottom of the flask to prevent the precipitate coming in contact with the air and being oxidized further.

When the iodine had been liberated the flask was disturbed as little as possible. The liquid was not stirred too violently during titration in order that iodine would not be lost by vaporization.

Care had to be taken that no air bubble was in the flask after the reagents were added and the precipitate was formed. If air entered it would increase the value of the solubility of the oxygen due to the further oxidation of the precipitate.

2. What Is the Precipitate?

Sodium hydroxide would precipitate manganous hydroxide when in contact with the manganous ion. We might consider that we had manganous acid formed (H_2MnO_3) by the contact of this precipitate with the oxygen in solution. Manganous acid forms a salt of manganous manganite, $MnMnO_3$ in the presence of excess manganous hydroxide. There might be some MnO_2 present also. As to what the definite composition was it could not be said but no matter what the composition, an equivalent amount of iodine would always be liberated by the higher state of oxidation of the manganese oxidizing the iodide to iodine.[21, 22]

$$O_2 + 2Mn(OH)_2 = 2H_2MnO_3$$
$$2H_2MnO_3 + 2Mn(OH)_2 = 2MnMnO_3 + 4H_2O$$

VI. EFFECT OF SIPHONING.

There was a possible loss of oxygen due to the transfer from one vessel to another by siphoning. A simple apparatus was constructed consisting of an Erlenmeyer flask (A) and the determination flask (B). In the flasks were two hole stoppers and glass tubing. Both flasks were filled with gas free water.

Part of the water was displaced from A by inverting the flask when oxygen is passed in. About half the capacity of A was emptied of water. By inverting B in the same manner and continuing to pass oxygen in the apparatus about one-half of B was emptied. By shaking both flasks in a thermostat and still passing oxygen through, saturation was obtained under the same conditions in both flasks. After attaining equilibrium, flask B was filled by inverting A and forcing the water from A into B. The reagents were added to B. Solubilities were obtained as given in Table 8. Taking all precautions into consideration the solubility as expressed in Table 8 can be considered the solubility of oxygen as determined by this method.

TABLE 8.

cc. of Thiosulfate	Capacity of Flask	Barometer correct	Grams O_2 per liter
(.001577 g.)			
48.06	307.8	749.7	.04084
47.87	307.8	747.6	.04080
47.60	307.8	748.2	.04054
47.82	307.8	747.7	.04075
47.85	307.8	746.8	.04083
47.85	307.8	745.2	.04092
49.63	307.8	758.7	.04092
(.001676 g.)			
46.53	307.8	758.0	.04086
46.67	307.8	757.8	.04079
46.40	307.8	757.6	.04072
46.47	307.8	757.0	.04082
46.53	307.8	756.6	.04089
		Av.	.04080
		a. d.	$.0_4 73$
		A. D.	$.0_4 21$

These solubilities were carried out at a temperature of twenty-five degrees Centigrade.

The advantage in using this form of saturation apparatus was that at no time was any oxygen saturated water allowed to flow from one vessel to another unless in an atmosphere of oxygen and that atmosphere under a pressure at which the

saturation took place. In this way no oxygen could be lost from solution and the solubility obtained was in approximate agreement with those reported in the literature. The solubility as found herein was 0.04080 grams of oxygen per liter of water.

By comparing the average of the grams of oxygen per liter in Table 9 with grams per liter of oxygen in Table 8 it is noticed that there is a loss of oxygen due to siphoning. The solubility obtained when siphoning is used appears to be about three percent lower than the solubility obtained when saturated in the above manner as described. There was a constant loss of oxygen when the solutions were siphoned as Table 9 indicates.

TABLE 9.

cc. of Thiosulfate	Capacity of Flask	Barometer correct	Grams O_2 per liter
(0.00318 g.)			
22.90	307.8	750.5	.0392
23.30	309.8	750.5	.0395
23.00	307.8	750.5	.0394
23.00	307.8	751.3	.0393
23.35	309.8	751.3	.0395
23.00	307.8	751.3	.0393
23.50	309.8	752.2	.0397
23.30	307.8	752.2	.0398
23.15	307.8	752.2	.0395
(0.003227 g.)			
23.30	307.8	768.1	.0395.
23.60	309.8	768.1	.0396
23.30	307.8	768.1	.0398
22.80	309.8	749.7	.0392
22.40	307.8	749.7	.0389
23.35	309.8	754.2	.0399
22.95	307.8	754.2	.0396
22.95	307.8	754.2	.0396

The solubilities were carried out at a temperature of twenty-five degrees centigrade. These solutions were siphoned into the determination flask.

The formula for calculation to 760 mm. when 100 cubic centimeters of the liberated iodine solution were taken from the flasks and reagents added as per method was as follows:

$$\frac{\text{cc. of thiosulfate} \times \text{to 1 cc. thiosulfate} \times 760 \times \text{capacity flask}}{\text{Flask capacity} - 100 \text{ cc.} \times \text{Barometer} - \text{v.p.} \times \text{cap. of flask}}$$

Grams of O_2 equiv.

Corrected

minus reagents added

This formula of calculation gave the grams of oxygen in one liter of water at one atmosphere pressure. This is the value "q."

VII. EXPRESSING THE SOLUBILITY.

As a more practical means of expressing solubility of oxygen in water, it was thought that if the solubility were expressed in grams per thousand cubic centimeters of water when the partial pressure of oxygen is 760 mm. a method of expression would be approached that would not lead to as much confusion as when cubic centimeters and other coefficients are used. Calculating the changes in the volume of the gas was avoided when the value was expressed in grams. The solubility could be calculated directly from the grams of oxygen equivalent to one cubic centimeter of the standard thiosulfate solution. A value for the solubility was obtained when the partial pressure of the oxygen was 760 mm. which could be used as a standard when the solubilities were determined at various pressures. The vapor pressure would then not interfere with comparison at various pressures, as it would if the solubility was expressed as the partial pressure of the oxygen plus the vapor pressure totaling 760 mm.

As a means of comparison, the values of the solubility as expressed by various workers are shown in Table 10.

1 is the Ostwald coefficient defined as the ratio of the volume of gas absorbed at any pressure and temperature, to the volume of the absorbing liquid.

b is the Bunsen absorption coefficient. It is defined as the volume of the gas at 0° C and 760 mm. taken up by unit vol-

TABLE 10.

Comparative Values.

Observer	l	b′	b	q	q′
Richardson	.03021	.02765	.02854	.04080	.03950
Pyne[16]	....	....	.02833	.04047	.03922
Carlson[23]	....	....	.02867	.04097	....
Fox[24]	....	....	.0289	.0413	....
Bohr & Bock[25]	....	....	.02904	.04149	....
Dittmar[26]	....	....	.02857	.04081	....
Winkler[27]	....	.02756	.02844	.04063	....
Winkler[28]	....	.02743	.02831	.04045	.0393
Roscoe & Lunt[29]	....	.02748	.02820	.04028	....
Thresh[30]	....	.02729	....	.04023	....
MacArthur[31]	....	.02758	....	.04066	....
Hüfner[32]	....	.02745	....	.04047	....
Geffcken[33]	.03080	....	....	.04151	....
			Av.	.04074	

ume of liquid when the pressure of the gas itself minus the vapor tension of the solvent is 760 mm.

b′ is often used and is defined as the volume of gas at 0° C and 760 mm. which is absorbed by unit volume of the liquid at a barometric pressure of 760 mm.

q is the weight of the gas in grams absorbed by 1000 cc. of solvent at a definite temperature and a total pressure of 760 mm. (Partial pressure of gas = 760 mm.) This is the coefficient used in this work.

q′ is the same as q but the barometer reading is 760 mm. Vapor tension is not taken into consideration.

VIII. SOLUBILITY OF OXYGEN AT PRESSURE LOWER THAN ATMOSPHERIC.

Henry's Law has always been taken as an approximation in the case of most gases. Little experimental evidence has been evinced for its validity although many investigations have been carried out. Here an analytical method will be applied to the solubility of oxygen at pressures less than atmospheric in pure water.[16, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47]

An apparatus (Fig. 1) was designed whereby the liquid could be saturated by shaking at a measured pressure less than atmospheric. The apparatus was designed in such a way that

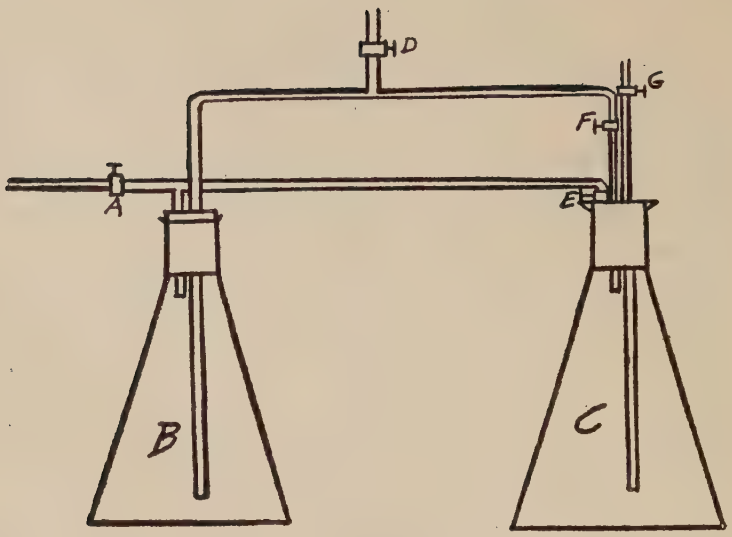


Figure 1

the liquid could be transferred from one vessel to another in an atmosphere of oxygen and under the pressure at which it was saturated.

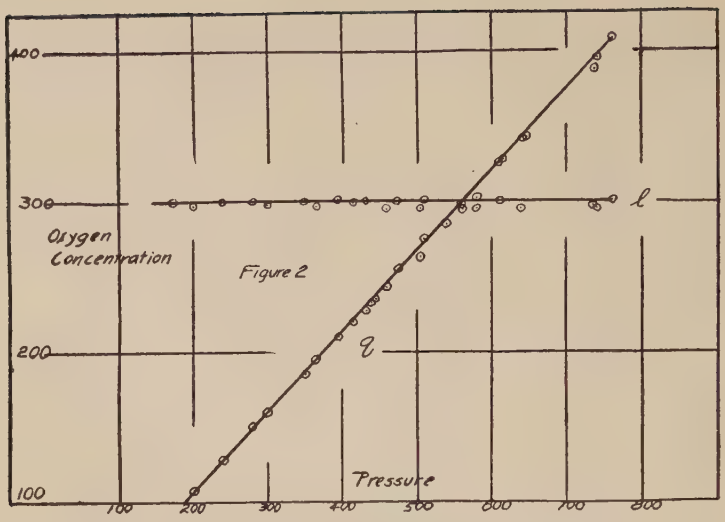
Flasks B and C were filled with gas free water. This was siphoned into the flask with as little exposure to the air as possible. The apparatus was filled with oxygen before placing the flasks in position. At first the flasks were sealed at the stoppers with collodion but it was found that this was not necessary. The rubber stopper gave sufficient airtightness. Stopcock E was closed. Oxygen was allowed to enter through A forcing water from B to C. About half the contents of B was emptied. The water escaped from flask C at G which was open. Then E was opened and F closed. The water from C was allowed to escape through G. E was opened. Our system was then at atmospheric pressure. Suction was placed on A to the approximately desired pressure. Flask B and C were shaken in the thermostat. The liquids were allowed to come to equilibrium and the manometer was read. With E and F open, B was inverted and the contents of the flask B allowed to

fill flask C. E and F were closed. Flask C was removed from the apparatus. The reagents were immediately added as described above.

TABLE 11.

Reduced press.	Grams O_2 per liter	1	K = G/P
174.7	0095	2999	5329
202.2	0107	2978	5302
240.7	0128	2993	5318
242.5	0128	2970	5258
280.7	0150	3007	5333
300 3	0160	2998	5318
349.0	0184	2967	5278
364.1	0196	3030	5378
396.1	0210	2984	5292
413.7	0220	2992	5306
433.3	0227	2948	5246
440.5	0233	2976	5289
446.7	0235	2961	5267
458.3	0243	2984	5304
478.1	0254	2991	5315
504.8	0265	2954	5253
511.4	0273	3005	5340
539.7	0283	2951	5244
559.3	0295	2968	5277
577.7	0303	2952	5252
610.2	0325	2998	5323
614.6	0327	2994	5324
639.7	0337	2964	5270
649.2	0342	2965	5273
738.7	0387	2948	5239
741.1	0394	2992	5307
741.1	0393	2984	5307
	Av.	2980	5294
	A. D.	$.0_4 3$	$.0_3 55$
	a. d.	$.0_3 15$	$.0_2 28$

Here it will be seen that the solubility follows Henry's Law. Referring to Figure 2, the solubility follows a straight line. Pressure was plotted against solubility in grams per thousand cubic centimeters and from this it was evident that the Law of Henry held at these lower pressures of oxygen. Looking at



the last column in Table 11, it was observed that the number obtained by dividing the grams per thousand cubic centimeters by the pressure is constant.

In the column next to the last are given the solubilities of oxygen expressed as the Ostwald solubility coefficient. These values were calculated by the following formula,—

$$1 = \frac{224 \times 298 \times 736.5 \times q}{3200 \times 273 \times P}$$

where q is the grams of oxygen per 1000 cc. and P is the pressure at which the solution was saturated. The Ostwald solubility coefficient is also plotted on Figure 2 against pressure. It will be seen that the values fall on a straight line which is parallel to the pressure axis. Hence it can be considered that oxygen obeys Henry's Law when pressures are considered between 175 mm. to 760 mm. of mercury.

IX. DISTRIBUTION EXPERIMENTS.

Some experiments to determine the coefficient of distribution of oxygen between water and liquids partially miscible

with it were carried out. Water boiled free of gases was used. The liquid to be used with it was boiled under reduced pressure for one-half hour, but at room temperature.

The gas free water was shaken in a 1000 cubic centimeter flask in a thermostat at twenty-five degrees Centigrade. The water was shaken with oxygen for fifteen minutes. The total amount of oxygen in solution was then known. The value taken from the averages of determinations was 0.04080 grams of oxygen per liter of water, — the solubility of oxygen at 25° C.

A measured quantity of the organic liquid was placed in a calibrated flask with glass stopper, the capacity of which was known when completely filled and the glass stopper in place. The remainder of the space in the flask was immediately filled with water saturated with oxygen at the temperature twenty-five degrees and pressure of the atmosphere. The water was siphoned into the flask with as little disturbance of the liquid as possible so as to avoid any loss of oxygen by excess movement or break in the surface of the liquid. The stopper was placed in the flask so that no air was included. The liquids in the flask were allowed to come to the temperature of the thermostat (25° C.) they being within at least a degree of the temperature when first placed in the bath. Having assumed the temperature, they were shaken at approximately five-minute intervals from one-half hour to one hour. This allowed the organic liquid which was considered free from oxygen to extract from the saturated water solution, the oxygen therein dissolved. After this extraction, the water layer was siphoned into regular iodine flasks which have been described and in which the titration was carried out. The procedure as given for oxygen was used and the amount of oxygen found in the water layer determined.

Benzene, toluene, chloroform, carbon tetrachloride, bromoform, ethyl benzene and anisole were used for extracting oxygen from the water solution.

With several liquids namely, benzene, toluene, and chloroform different volumes of the extracting liquid were tried and it was found that a constant was not obtained. The coefficient

TABLE 12.

Volume of organic solvent	Volume of water	Coefficient	Average
Benzene			
100	900	8.26	
		8.26	
		8.67	
		8.74	8.48
200	800	7.10	
		7.23	
		7.31	
		7.67	
		7.68	7.39
300	700	7.19	
		7.19	
		7.25	
		6.91	
		7.20	
		7.12	
		7.22	7.15
400	600	6.52	
		6.49	
		6.39	
		6.39	6.45
500	500	5.47	
		5.11	
		5.51	
		5.58	
		5.33	
		5.25	
		5.46	
		5.48	5.40
100	400	5.53	
		5.27	
		5.39	
		5.24	
		5.36	
		5.37	5.34
50	450	6.01	
		5.72	
		5.96	
		6.16	
		6.24	
		6.21	6.05
175	825	6.96	
		7.25	7.11

TABLE 12—Continued

Volume of organic solvent	Volume of water	Coefficient	Average
Carbon Tetrachloride			
100	400	7.22	
		7.43	
		8.18	
		7.81	
		6.94	
		7.58	
		8.06	
		7.62	
		7.62	
		8.18	7.67
Toluene			
100	400	4.65	
		4.69	
		4.73	
		5.09	
		5.24	
		5.36	
		5.26	
		5.29	5.09
50	450	5.90	
		5.75	
		6.03	
		6.06	5.94
Chloroform			
100	400	6.58	
		6.68	
		6.55	
		6.45	
		6.42	6.54
50	450	7.46	
		7.17	
		7.42	
		7.17	7.31
500	500	7.42	
		6.74	
		6.35	6.84
Bromoform			
50	450	2.67	
		2.84	
		2.92	
		2.79	2.81

TABLE 12—Continued

Volume of organic solvent	Volume of water	Coefficient	Average
Ethyl Benzene			
100	400	4.27	
		4.18	
		4.33	
		4.24	4.30
Brom Benzene			
100	400	4.71	
		4.11	
		4.08	
		4.02	
		3.78	
		3.91	3.87
Anisole			
100	400	3.76	
		3.88	
		3.62	
		3.99	3.81

reported in Table 12 is the moles of oxygen in the organic liquid divided by the moles of oxygen in the water. A constant was obtained when the same concentrations were used but when different concentrations were used the coefficient did not remain the same. In the cases of benzene, toluene and chloroform the coefficient was larger in all cases when 50 cubic centimeters of extracting liquid was used than when 100 cubic centimeters was used. There seems to be no evident reason for this result other than that equilibrium was not obtained. The largest error would be in the siphoning process after the oxygen had been distributed. It is here that many of the errors creep in. These errors however would not be sufficiently large to account for the wide discrepancies in the constants.

As another means of getting a different concentration of oxygen to extract, water was saturated with benzene and chloroform. This was then saturated with oxygen. Distribution was then carried out in the same manner as the original distribution experiments described.

In these experiments the coefficient for benzene was 4.86 and for chloroform 5.98. These are lower than those obtained

in Table 12. Experiments were carried out to determine whether the time allowed for distribution was of sufficient length. Benzene and water were allowed to remain in contact with occasional shaking for from one hour to fifty-three hours. The volume of benzene and water was each 500 cubic centimeters. There seemed to be no difference in the value obtained for the constant for longer periods than when one-half hour was allowed for distribution.

From these data it seemed impossible to obtain a constant distribution coefficient.

X. SOLUBILITY OF OYGEN IN WATER SOLUTION OF PHENOL.

To apply the method further, solutions of phenol and water were made of concentrations, .05 M., 0.1 M., 0.2 M., 0.3 M., 0.35 M., and 0.4 M. These solutions were made from gas free water and pure phenol of Eimer & Amend. The gas free water was placed in a calibrated liter flask. A weighed amount of phenol was placed in the flask which was filled with the liquid to the glass ground stopper. Phenol was dissolved by shaking. The solution of phenol was siphoned into a pyrex one liter balloon flask into which oxygen was introduced by a jet below the surface of the solution. The solution completely filled the flask. A space filled with oxygen above the liquid was created by displacing some of the phenol solution by the incoming oxygen gas. After creating an atmosphere of oxygen above the solution, the flask was shaken for fifteen minutes in the thermostat at twenty-five degrees. Allowing this solution to come to equilibrium, the solution of oxygen in phenol and water was siphoned into the usual determination flasks. The reagents were added as advocated above and the procedure carried out similarly.

When higher concentrations of phenol were used, results were not to be relied upon because the concentration of the phenol reached such a high value that it evidently interfered with the reagents in some way. No checks could be obtained on the various results. The possible explanation for the inac-

TABLE 13.

Molarity of Phenol	Grams per 1000	Average
.05299	0362	
	0358	0360
.05257	0362	
	0351	0356
.05294	0357	
	0344	0351
.05166	0371	
	0366	0368
.05254		0359
.1078	0353	
	0347	
	0357	0352
.1055	0351	
	0349	0350
.1028	0338	
	0353	0346
.0981	0344	
	0344	0344
.1036		0344
.2326	0337	
	0336	0337
.2330	0338	
	0324	0331
.2330		0334
.2061	0325	
	0312	0319
.2041	0333	
	0322	0328
.2051		0317
.3622	0285	
	0315	0300
.3607	0299	
	0299	
	0361	0330
.3615		0315

TABLE 13—Continued

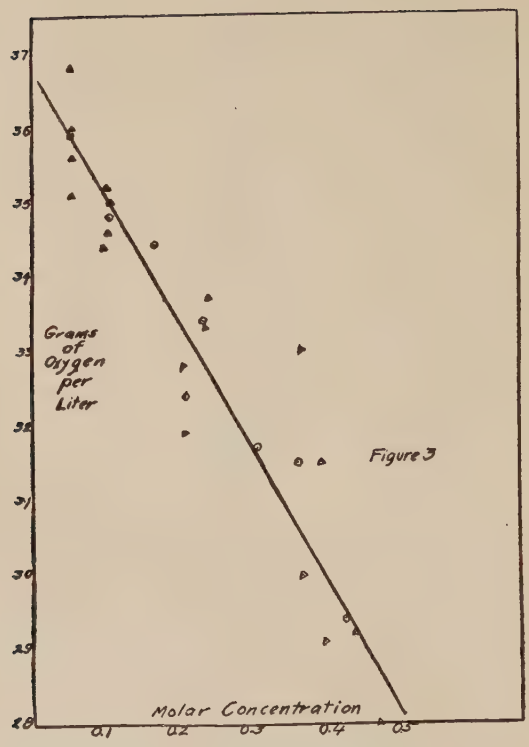
Molarity of Phenol	Grams per 1000	Average
.3849	0302	
	0326	0314
.3908	0289	
	0293	0291
.4275	0296	
	0288	0292
.4662	0277	
	0282	0280
.4174		02941
.3003	0313	
	0322	0317
.1638	0345	
	0342	0344

curacy of results when higher concentrations of phenol were used was that salts of phenol were formed to such an extent that the concentrations of the reagents were seriously interfered with and thereby the inconsistency. There were larger errors in the plotted results than in the determination of the solubility of oxygen in pure water.

From the diagram it can be seen that the results will lie on a straight line when grams of oxygen per liter are plotted against the concentration of the phenol in water solution. The results plotted are averages. Two determinations of the solubility of oxygen were made in each concentration and these averaged. The averages of the approximate concentration were averaged. These values of the concentration of phenol and the grams of oxygen per liter were the values plotted in Figure 3.

XI. HYDROGEN PURIFICATION.

In electrolytic work with the hydrogen electrode, it has been found that oxygen poisons the electrode causing error in the results. Aten, Bruin & DeLange[48] used hydrogen which was tested for oxygen by passing the gas over phosphorus. No



cloud was formed in this sample of their hydrogen. They introduced in hydrogen 0.01% oxygen and with this concentration when passed over phosphorus, a slight cloud formed. The oxygen in their sample contained therefore less than 0.01% oxygen. To estimate the oxygen in their sample, 20 liters of the gas were passed through a solution of approximately the same composition which is used in this method. The oxygen is absorbed and they found 0.00001%. The work was not described well and this procedure was investigated.

Hydrogen gas was passed through the precipitating flasks which contained gas free water and a precipitate formed by adding the 5 cc. of NaOH and $MnSO_4$ and 5 cc. KI solution. Approximately 20 liters were passed through at a rate sufficiently rapid to cause stirring of the precipitate but not so rapid as to diminish the time for the oxygen to be absorbed by the

precipitate. The sample of hydrogen contained more oxygen than is usually found in tank hydrogen but the amount was not known.

After having passed the gas through the solution and precipitate to remove the oxygen, it was passed through a solution of alkaline pyrogallol. The solution did not remain colorless but gave the characteristic brownish red tint which is characteristic of the presence of oxygen. By merely bubbling the impure hydrogen through the precipitate, it will not be purified from oxygen sufficiently for hydrogen electrode work as indicated by the pyrogallol test on the gas after such a treatment. Oxygen was absorbed by the precipitate since on acidification the precipitate dissolved giving free iodine due to some of the higher state of oxidation of manganese being formed by oxygen being absorbed.

As a quantitative means of purification of hydrogen for electrode purposes this method does not seem applicable. Should the gas be passed and re-passed several times through the reagents, it is inevitable that all the oxygen would be removed but one treatment is insufficient.

XII. HYDROSTATIC PRESSURE.

When a gas was introduced under a column of water the pressure when the bubble was released at the bottom of the column was more than the pressure when the bubble reached the top of the column of water.

Winkler[2] suggested that hydrostatic pressure entered into the solubility relationship and considered half the column of water in the saturation of water with gas as the pressure due to the water. This pressure in his calculation was added to the atmospheric pressure and called the pressure under which the liquid was saturated. No work was done by him in this respect and not much emphasis was laid on this point. There has been no experimental proof of this assumption.

A glass column was constructed two meters and a half high. The diameter of this column was 7.4 centimeters. There were tap-offs at intervals of 58 centimeters. These tap-offs were

closed by rubber tubing and pinch clamps. Inside the column there were suspended funnels without stems which fitted the glass tube as closely as possible. The larger end was downward. These funnels were four in number. They were placed midway between the tap-offs. A capillary tube was run through the centers of these funnels. The opening of the small end of the funnel was sufficiently wide so that when a bubble rose in the liquid, it could pass easily through this aperture even with the capillary tubing running through it.

The purpose of the funnels was to prevent mixing. As the bubble rose from the bottom of the column the rise was halted by striking the side of the funnel thereby stopping much of the mixing. It then started from the center of the column in the next zone until it struck the funnel bounding the two zones.

The water was made gas free. This was introduced through the tap-off at the bottom of the column. The gas was bubbled through slowly in order to keep the mixing at a minimum. Saturation was carried out for varying periods of time. When the saturation time was up the gas was shut off and the first sample withdrawn from the top. The reagents were added immediately after the sample was withdrawn. The other samples were withdrawn successively from the top to bottom.

Glass funnels were suspended on hard rubber rings which fit the tube tightly. In Table 14 the solubility of oxygen at various depths is expressed. In all cases the solubility was increased with the height of the column of liquid. The values given in Table 14 show that there is definitely an increase in the solubility with an increase in hydrostatic pressure. It cannot be said that the solubility is proportional to the hydrostatic pressure for saturation had not been reached and until this condition was obtained results could not be comparable. When the samples were taken from the column and the reagents added, there was a loss of oxygen content of the water. Small bubbles were seen arising from the solution. The phenomena was more pronounced in the samples which were taken from the bottom of the column due to the greater pressure under which the water was saturated.

TABLE 14.

Height of Water cm.	Barometer Corr.	Grams 0_2 in 1000	Time in hours
0	736.9	0294	23.5
58	736.9	0347	23.5
116	736.9	0378	23.5
174	736.9	0390	23.5
232	736.9	0394	23.5
0	746.9	0344	31.5
58	746.9	0402	31.5
116	746.9	0428	31.5
174	746.9	0438	31.5
232	746.9	0448	31.5
0	755.7	0325	62.0
58	755.7	0421	62.0
116	755.7	0458	62.0
174	755.7	0468	62.0
232	755.7	0473	62.0
0	763.0	0315	22.5
58	763.0	0430	22.5
116	763.0	0457	22.5
174	763.0	0472	22.5

Another type of apparatus was constructed for determining what effect the hydrostatic pressure had upon the solubility of oxygen. Saturation was carried out by bubbling oxygen through a determination flask filled with water, to which was attached a column of liquid adjustable to any height. The oxygen was introduced at the bottom of the flask and under a pressure equivalent to the atmospheric pressure plus the hydrostatic pressure of the column of the liquid above the flask. In this way it was possible to saturate in the flask in which the final determination was carried out thereby saving the transfer of liquid and hence avoiding loss of gas due to the decrease in total pressure when hydrostatic pressure is released.

Glass tubing of bore 1.7 cm. was attached to iodine flasks. Through this tubing was an inner tube of 0.5 cm. bore for conducting the gas to the bottom of the iodine flask to the inner tubing extended from the bottom of the iodine flask to the top

of the outer tubing. A battery of four tubes and flasks were used for one saturation.

At the bottom of the tubes was attached a smaller length of tubing of the same bore as the outer tube. The shorter length, about 15 cm. long was connected to the longer length by gum rubber tubing of the same bore as the tubing. Screw clamps were used at the rubber connections to prevent the water in the column from running out on disconnecting from the flask.

Water for saturations was made gas free. The water was siphoned into the determination flasks. The flasks were attached to the column by inserting the rubber stopper which was attached to the end of the column. After closing the clamps at the bottom of the column, the column was filled with water, introducing it at the top. Having filled the column with water at various heights, the clamps were opened whereby the space between the clamps and the water in the flasks was filled with water. The inner tubing for the introduction of the was then lowered to the bottom of the flask. An even flow of oxygen was regulated in all flasks.

Oxygen was bubbled through for periods of twenty hours. This seemed to be the minimum time in which it could be certain that saturation was obtainable. At the end of this time the heights of the column of liquids were measured. The inner tubes were raised above the rubber connection and the upper part of the columns and flasks were separated by clamping. The flasks were then removed and reagents added in the quantities recommended in the Modified Winkler Method for Oxygen. The procedure was carried out as recommended with the exception of the following points:

Instead of introducing the sodium hydroxide solution before the manganese sulfate solution it was found that more accuracy could be obtained by introducing the manganese sulfate solution first. There was a noticeable evolution of gas when the sodium hydroxide was added. The solution being saturated at a higher pressure than atmospheric had a tendency to lose gas at atmospheric pressure. This loss of gas was noticeable only when the sodium hydroxide was added. If the sodium hydroxide was added as the last reagent before closing the

flask, there was little opportunity for the oxygen to escape as the bubbles rose too slowly. All the reagent could be added before the bubbles reached the neck of the flask. The stopper could be inserted before any oxygen could escape.

The temperature of the water was taken from a sample withdrawn from the lower section of the column next to the flask.

TABLE 15.

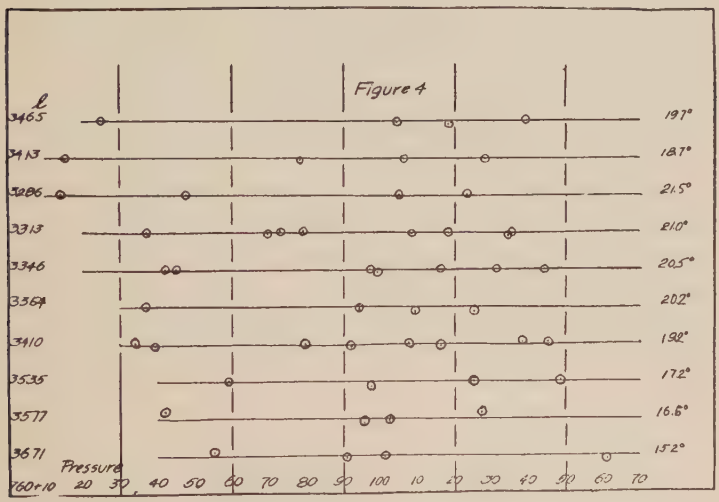
Mm. Hg minus flask	Total press. —760	Temp.	Grams O_2 per liter	Grams O_2 at 760	Solubility	1
92.4	72.7	21	04926	04392	04365	3331
98.7	79.0	21	04966	04395	04365	3331
127.8	108.1	21	05056	04328	04365	3277
153.8	134.1	21	05111	04251	04365	3218
72.8	42.6	20.6	04796	04377	04404	3362
127.2	97.0	20.6	05043	04320	04404	3312
129.8	99.6	20.6	04972	04247	04404	3255
161.7	131.5	20.6	05271	04346	04404	3328
78.3	41.8	16.6	05346	04847	04741	3754
132.1	95.6	16.6	05306	04520	04741	3490
138.7	102.2	16.6	05441	04601	04741	3502
163.5	127.0	16.6	05881	04840	04741	3732
61.4	34.1	19.2	04890	04524	04507	3465
107.0	79.7	19.2	05046	04423	04507	3388
134.8	107.5	19.2	05305	04506	04507	3441
165.0	137.7	19.2	05564	04511	04507	3488
60.2	55.4	15.2	05438	05016	04873	3753
95.7	90.9	15.2	05478	04865	04873	3623
106.1	101.3	15.2	05582	04898	04873	3647
165.9	161.1	15.2	05889	04891	04873	3598
69.1	59.0	17.2	05198	04765	04677	3572
107.6	97.5	17.2	05193	04549	04677	3408
135.0	124.9	17.2	05553	04715	04677	3532
158.7	148.6	17.2	05806	04803	04677	3595
52.4	39.5	19.2	04789	04483	04507	3372
105.1	92.2	19.2	05107	04483	04507	3373
129.4	116.5	19.2	05224	04464	04507	3355
158.1	145.2	19.2	05428	04493	04507	3453

TABLE 15—Continued

Mm. Hg minus flask	Total press. —760	Temp.	Grams O_2 per liter	Grams O_2 at 760	Solubility	1
40.9	14.4	21.5	04580	04346	04327	3331
74.2	47.7	21.5	04741	04320	04327	3303
131.3	104.8	21.5	05078	04330	04327	3305
149.8	123.3	21.5	05186	04332	04327	3305
54.6	44.9	20.4	04796	04579	04412	3352
106.8	97.1	20.4	05065	04441	04412	3325
125.5	115.8	20.4	05193	04457	04412	3338
154.0	144.3	20.4	05454	04451	04412	3332
52.8	37.0	21.0	04684	04380	04365	3309
85.4	69.6	21.0	04826	04339	04365	3273
133.9	118.1	21.0	05123	04355	04365	3284
150.9	135.1	21.0	05209	04346	04365	3275
60.2	36.8	20.2	04716	04370	04427	3331
117.2	93.8	20.2	05024	04352	04427	3312
132.8	109.4	20.2	05036	04287	04427	3260
148.3	124.9	20.2	05106	04272	04427	3247

Results of the experiments are given in Table 15. In Table 15, the second column gives the pressure in millimeters of mercury exerted by the column of water from the top of the flask to the level of the water in the column. This pressure plus the atmospheric pressure will give the total pressure on the liquid. The solubility of oxygen at the total pressure is given in column headed "Grams of O_2 per liter." In the column next to the last is the solubility of oxygen reduced to 760 millimeters according to Henry's Law. Comparing the reduced values for the solubility with the solubilities at various temperatures and 760 millimeters, the agreement is very pronounced. When the solubility of oxygen was calculated using the column of water from the bottom of the flask to the level of the water in the column, the solubility was low. Taking the pressure of the column of water exerted from the top of the flask to the level in the column, the agreement between the solubility of oxygen when reduced to 760 mm. by Henry's Law, and the reported solubilities at various temperatures is exceedingly close.

Due to the small bore tubing, mixing of the water in the column with the water in the flask was very slight. Since the error in these determinations is larger than when the solubility is determined at atmospheric pressure, it seems highly probable that the mixing although slight would cause this larger error. The saturations were not conducted in a thermostat. Slight error would be introduced by this in one direction or another as equilibrium could not be reached if there was a sudden change in the temperature. There were little changes in temperature although local drafts might cause a slight variation. The error is not sufficiently large to prevent arriving at the conclusions. (Fig. 4)



In Figure 4, the pressure of the column of water in millimeters of mercury when measured from the top of the flask is plotted against 1, the Ostwald Coefficient at the temperature indicated. These points give a straight line for each temperature parallel to the pressure axis. From these solubilities with varying heights of water above, it can be concluded that the solubility of oxygen is proportional to the hydrostatic pressure above the solution providing there is no mixing.

Winkler was correct in assuming that the solubility at a greater depth was larger than at the surface, for the hydrostatic pressure acts in the same manner on the solubility of gases as the atmospheric pressure. In vessels where we have mixing it is not necessary however to take one half the hydrostatic pressure and add it to the atmospheric pressure in calculating the solubility. In cases of mixing, the height of the water column is considered as zero. When the column of liquid two and a half meters in height was saturated, it could be seen that the difference in the amount of oxygen in the bottom of the column and that at the top was very small. Even when means were taken to prevent undue stirring this difference was small. With even the slightest stirring the solubility difference between the top and bottom seemed quite small. With a flask ten centimeters high, the height of the column would have little effect on the solubility. This is especially true when the oxygen is dissolved in the water by shaking methods. The part that is supersaturated in respect to the atmospheric pressure establishes an equilibrium with the atmospheric pressure thereby losing its excess oxygen. Since there is no more oxygen available to saturate the lower layers, the lower layers become of the same composition as the upper layers and there is a uniform concentration of oxygen saturated at atmospheric conditions.

XIII. SUMMARY.

1. The Winkler Method for determining oxygen solubility is not applicable when oxygen is used instead of air.

2. An analytical method for the determination of the solubility of oxygen has been developed. This is a modification of the Winkler Method using oxygen instead of air.

3. Larger concentrations of the reagents are necessary for the determination of the solubility of oxygen than in the Winkler Method. With small concentrations lower values for the solubility of oxygen were obtained. The proper concentrations have been found for high concentrations of oxygen in solution.

4. The solubility for oxygen in water has been determined at 760 mm. and 25° C. by the modified method and found to be 0.04080 grams of oxygen per liter of water. The value is in agreement with values by other workers who measured the loss of volume of the gas when brought into intimate contact with water.

5. Considerable oxygen was lost upon siphoning saturated solutions of oxygen in water. An apparatus to eliminate this loss has been described.

6. The solubilities of oxygen in water at pressures from 175 mm. to 760 mm. at 25° C. have been determined and found to conform to Henry's Law.

7. Experiments failed to determine a constant distribution coefficient for oxygen between organic liquids and water.

8. The solubility of oxygen in concentrations of phenol in water from 0.05 M to 0.4 M decreased with increasing concentration of phenol.

9. The method as a means of purifying hydrogen for electrode work did not prove satisfactory.

10. The solubility of oxygen in water was found to be proportional to a column of water above it, thereby making the solubility proportional to the hydrostatic pressure exerted by this column of water.

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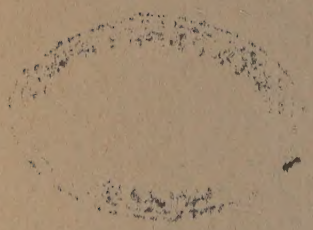
XV. VITA.

Alan H. Richardson was born in New Brunswick, New Jersey, on August 13, 1901. Attended the Public Schools in New Brunswick, N. J., graduating from New Brunswick High School in 1919. Graduated from Rutgers University in 1923 with the degree of B.S. Entered Columbia University in 1923. Was Assistant in Chemistry at Columbia University 1923-1927. Instructor in Inorganic Chemistry at Columbia University 1928. He is a member of Phi Lambda Upsilon, the Society of Sigma Xi, and the American Chemical Society.

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